662. *The Fate of Methyl Radicals in the Mechanism of Thermal Decomposition of Metal Alkyls.*

By L. H. Long.

Study of the observed methane : ethane ratios for the products of decomposition of AgMe, $CdMe_2$, $HgMe_2$, $SiMe_4$, $SnMe_4$, $PbMe_4$, and $AsMe_3$ reveals that, whereas at high temperatures the ratios become erratic, at lower temperatures they appear to be essentially independent of the nature of the decomposing metal alkyl (as well as, to a first approximation, of the pressure and fraction decomposed), a maximum being observed at ~340°. This casts doubt on the correctness of the usual assumption that the methane arises through interaction of methyl radicals with further metal alkyl molecules.

The observations, as well as a number of others from recent work on the pyrolysis of dimethyl-mercury and -cadmiun, can be explained with greater economy of hypothesis by a mechanism in which the methane arises through the reaction of methyl radicals among themselves, not on a first collision but in a series of subsequent steps, all of which are to be associated with more favourable activation energies and steric factors.

ALTHOUGH a variety of mechanisms of pyrolysis have been proposed for a number of metal alkyls, no comprehensive theory has so far been propounded. It has frequently been *assumed* that the alkyl radicals liberated by the initial decomposition are completely accounted for by hydrogen-abstraction reactions with further molecules of the compound being pyrolysed, in the manner not uncommonly observed in the case of other kinds of organic compounds. Evidence recently obtained from studies of dimethylmercury [1] and dimethylcadmium [2] do not accord with such an assumption, however, so that a fresh examination of the available facts concerning the other metal alkyls is timely. For simplicity, attention is here restricted to methyl compounds. No claim is made that this paper in any way establishes a new general decomposition scheme for metal methyls, but certain regularities are pointed out for the first time, while the mechanism suggested is able to explain the observed data in a simple and reasonable manner.

The Available Evidence.—The results of all investigations of metal methyls in the vapour phase so far published in suitable form and with sufficient detail for useful comparison are included in Table 1. (Further data are available for dimethylcadmium,[13] but are erratic through a pronounced surface effect and are not expressed in a suitable form.) Only results of pyrolysis studies in " static " systems are tabulated, as the flow technique demands excessively high temperatures and fast rates of reaction. Also excluded are the results of experiments in which <1% decomposition was effected or in which the metal alkyl vapour

---

[1] Laurie and Long, *Trans. Faraday Soc.*, 1955, **51**, 665.
[2] Laurie and Long, to be published.

was adulterated. As the temperature region below 250° is not represented by any vapour-phase pyrolysis data, one result for solid methylsilver at —40° in an inert solvent, and a series of photolysis results for dimethylmercury over the range 100—240° have been added. The composition of the decomposition products from photolyses is materially dependent on the intensity of irradiation, so that only low-intensity runs are included in Table 1, these most nearly resembling the conditions of low radical concentration obtaining in " static " pyrolysis systems.

TABLE 1. *Pyrolysis of metal alkyls. Content of methane and ethane in gaseous products.*

Alkyl	Temp.	No. of runs averaged	Initial concn. (mmole/l.)	% decomposed	% CH_4	% C_2H_6	CH_4/C_2H_6	Ref.
* $AgMe$	—40°	—	—	100	0	100	0·00	3
† $HgMe_2$	100	1	1·6	1·8	4	96	0·04	4
† $HgMe_2$	125	2	1·6	2·0	9	91	0·1	4
† $HgMe_2$	150	1	1·6	2·0	17	83	0·2	4
† $HgMe_2$	175	1	1·6	1·9	25	75	0·3	4
† $HgMe_2$	200	1	1·6	2·2	39	61	0·6	4
† $HgMe_2$	240	1	1·6	3·0	59	41	1·4	4
$CdMe_2$	258	4	4·7	46	69	26	2·7	2
$PbMe_4$	265	1	24	?	65	22	3·0	5
$PbMe_4$	295	1	35	high	69	23	3·0	5
$AlMe_3$	298	2	5·4	22	98·6	1·4	70	6
$HgMe_2$	302	1	1·4	45	73 ‡	27 ‡	2·7 ‡	7
$HgMe_2$	303	6	2·2	23	93	3	31	1
$HgMe_2$	305·5	4	2·3	13	69	12	5·8	8
$HgMe_2$	312	1	0·8	100	75	24	3·1	9
$AlMe_3$	313	1	1·7	27	92	3	31	6
$PbMe_4$	315	1	34	high	79	16	4·9	5
$HgMe_2$	323·5	2	3·0	13	68	13	5·2	8
$HgMe_2$	330	1	0·8	100	77	23	3·3	9
$AlMe_3$	334	2	1·6	62	97	1·5	65	6
$PbMe_4$	340	1	35	high	86	8	11	5
$HgMe_2$	342	5	2·3	28	65	17	3·8	8
$HgMe_2$	346	5	2·2	36	80	14	5·7	1
$HgMe_2$	348	2	2·4	73	85	15	5·7	7
$HgMe_2$	350·5	1	0·8	100	77	23	3·3	9
$PbMe_4$	365	1	48	high	82	12	6·8	5
$HgMe_2$	370	1	0·8	100	71	30	2·4	9
$HgMe_2$	385	1	0·7	100	66	34	1·9	9
$PbMe_4$	395	1	46	high	74	19	3·9	5
$HgMe_2$	401	1	0·7	100	60	40	1·5	9
$AsMe_3$	410	1	4·3	100	91	5	18	10
$AsMe_3$	440	2	3·0	100	88	7	12	10
$PbMe_4$	440	1	18	high	52	39	1·3	5
$SnMe_4$	485	4	2·1	57	83	0	∞	11
$PbMe_4$	550	1	14	100	23	23	1·0	5
$PbMe_4$	620	1	18	100	28	20	1·4	5
$SiMe_4$	659	1	?	?	58	0	∞	12
$SiMe_4$	689	2	?	?	59	0	∞	12

* Solid methylsilver suspended in methanol. † Photolysis runs (low intensity).
‡ Accuracy stated to be low.

The pyrolysis results mostly lie in the range 250—450°. The initial pressures of vapour employed have, for easier comparison, been converted into concentrations (col. 4), while

---

[3] Semerano and Riccoboni, *Z. phys. Chem.*, 1941, *A*, **189**, 203.
[4] Rebbert and Steacie, *Canad. J. Chem.*, 1953, **31**, 631.
[5] Simons, McNamee, and Hurd, *J. Phys. Chem.*, 1932, **36**, 939.
[6] Yeddanapalli and Schubert, *J. Chem. Phys.*, 1946, **14**, 1.
[7] Cunningham and H. S. Taylor, *ibid.*, 1938, **6**, 359.
[8] Yeddanapalli, Srinivasan, and Paul, *J. Sci. Ind. Res. (India)*, 1954, **13**, *B*, 232.
[9] Pellin, Thesis, University of Connecticut, 1953; Univ. Microfilms (Ann Arbor, Michigan), Doctorial Dissertation Series, Publ. No. 6336.
[10] Ayscough and Emeléus, *J.*, 1954, 3381.
[11] Waring and Horton, *J. Amer. Chem. Soc.*, 1945, **67**, 540.
[12] Helm and Mack, *ibid.*, 1937, **59**, 60.
[13] Heller and H. A. Taylor, *J. Phys. Chem.*, 1953, **57**, 226.

the extent to which the decomposition had been allowed to proceed is indicated in col. 5. Cols. 6 and 7 reproduce the molar % of methane and ethane, respectively, in the gaseous products (solids and condensable substances being ignored for this purpose), and col. 8 gives their ratio.

Discussion.—The results being viewed as a whole, it is apparent that the percentages of methane and ethane in the gaseous products depend mainly on temperature, and are almost independent of concentration (which varies by a factor of ~50), of the percentage decomposition, and—except in a few runs—even of the nature of the metal alkyl at temperatures up to about 350°.

The three results for trimethylaluminium exhibit anomalously high methane : ethane ratios. The reason for this is not far to seek. Whereas all the other methyl compounds listed are believed to decompose by a first-order law, the decomposition of trimethylaluminium accords[6] with an order of 1½. That this difference in order is genuine is supported by the observation that the gaseous products of photolysis of trimethylaluminium at 29° and at 120° include unusually large proportions of methane, namely 26 and 43% respectively, while photolysis near room temperature of other metal methyls yields almost pure ethane with only very little methane. This suggests that trimethylaluminium, in contrast to the other metal methyls considered here (see later), has a low activation energy for the hydrogen-abstraction reaction :

$$CH_3 + Al(CH_3)_3 \longrightarrow CH_4 + (CH_3)_2AlCH_2$$

a fact immediately explicable in terms of the pronounced acceptor properties of aluminium, which would facilitate attack at the central atom, particularly by a radical possessing a non-bonding electron. The only other outstandingly high methane : ethane ratio appearing in the Table is that for dimethylmercury at 303° due to Laurie and Long,[1] but a different explanation is found for this (see later).

In view of the various experimental conditions and the approximate nature of some of the results—many of them do not even rest on a full gas analysis—the degree of concordance exhibited up to about 350° is striking. Trimethylaluminium being ignored, the variation observed in the proportions of methane and ethane produced on passing from compound to compound is no greater than that for the single compound most studied, namely dimethylmercury. As the temperature rises, the proportion of ethane—which at lower temperatures is almost the exclusive product—decreases while that of methane increases until it reaches a maximim value of ~80—90%. Just below 350° the trend is reversed and at appreciably higher temperatures the proportions of both methane and ethane become erratic and unpredictable, exhibiting in this temperature region an obvious dependence on the nature of the metal alkyl decomposing. At the same time other gases such as hydrogen and acetylene frequently appear in important amounts. The trend in the methane : ethane ratio is more easily seen in Table 2, in which the results of two series of experiments are separated. Although they refer to two different compounds and the pressures employed in one case are about 50 times those in the other, the maximum in the ratio occurs at the same temperature, namely about 340°.

TABLE 2. *Variation of methane/ethane ratio with temperature.*

(*a*) $HgMe_2$, concn. 0·71—0·82 mmole/l. After Pellin[9]

Temp.	% CH_4	% C_2H_6	CH_4/C_2H_6
312·0°	75·4	24·3	3·22
330·0	76·5	23·3	3·28
350·5	76·9	23·0	3·34
370·0	70·9	29·8	2·38
384·8	66·0	33·9	1·95
401·0	59·6	40·1	1·49

(*b*) $PbMe_4$, concn. 14—48 mmole/l. After Simons *et al.*[5]

Temp.	% CH_4	% C_2H_6	CH_4/C_2H_6
265°	65·1	21·7	3·0
295	68·9	22·9	3·0
315	78·5	15·7	5·0
340	86·1	7·8	11·0
365	82·2	11·6	7·1
395	74·2	18·5	4·0
440	51·9	38·9	1·3
550	22·6	22·6	1·0
620	27·7	19·9	1·4

These observations strongly suggest a common circumstance, namely that below this temperature the formation of methane and ethane is to be accounted for by the interaction of the methyl radicals alone without any important contribution from hydrogen-abstraction processes involving undecomposed metal alkyl molecules. No other assumption will explain all the facts with such economy of hypothesis.

That this assumption is in direct contrast to the assumptions usually made is most readily seen by reference to the mechanisms previously proposed for dimethylmercury. All workers agree that in both pyrolysis and photolysis methyl radicals are split off, either simultaneously or in successive steps, and that a good proportion of them combine to form ethane:

$$\begin{aligned} Hg(CH_3)_2 &\longrightarrow CH_3 + HgCH_3 \\ HgCH_3 &\longrightarrow CH_3 + Hg \\ 2CH_3 &\longrightarrow C_2H_6 \end{aligned}$$

There is no reason to doubt the correctness of this. However, even for the temperature region below 340°, it is usually assumed, without proof, that the observed methane is produced by interaction of methyl radicals with further dimethylmercury molecules:

$$\begin{aligned} CH_3 + Hg(CH_3)_2 &\longrightarrow CH_4 + CH_2{\cdot}Hg{\cdot}CH_3 \\ CH_3 + CH_2{\cdot}Hg{\cdot}CH_3 &\longrightarrow C_2H_5{\cdot}Hg{\cdot}CH_3 \\ 2CH_2{\cdot}Hg{\cdot}CH_3 &\longrightarrow (CH_2{\cdot}Hg{\cdot}CH_3)_2 \end{aligned}$$

One obvious difficulty is that at, say, 300° the main product is methane but the reaction is still of first order and hence not a chain reaction. In this mechanism it is therefore necessary further to assume that the $CH_2{\cdot}Hg{\cdot}CH_3$ radicals do not decompose to liberate methyl radicals—for this would establish a radical chain mechanism incompatible with the observed order of reaction—but survive until they combine with a methyl or secomd $CH_2{\cdot}Hg{\cdot}CH_3$ radical, as indicated. A second suggestion which has been made in attempting to account for certain photolysis results not entirely explicable by the foregoing mechanism is that methyl radicals and dimethylmercury molecules also form an "addition complex" which then reacts further:

$$\begin{aligned} CH_3 + Hg(CH_3)_2 &\rightleftharpoons CH_3{\cdot}Hg(CH_3)_2 \\ CH_3 + CH_3{\cdot}Hg(CH_3)_2 &\longrightarrow \textit{either}\ C_2H_6 + Hg + 2CH_3 \\ &\qquad\ \ \textit{or}\ \ C_2H_6 + HgCH_3 + CH_3 \\ &\qquad\ \ \textit{or}\ \ C_2H_6 + Hg(CH_3)_2 \end{aligned}$$

Again it is necessary to suppose that the "addition complex" $CH_3{\cdot}Hg(CH_3)_2$ survives and does not react until it encounters another methyl radical.

Neither of these two sets of assumptions, which have been made to avoid postulating a chain mechanism, is satisfactory from the standpoint of economy of hypothesis. A second objection is that the only methane-producing process proposed is one which involves the abstraction of a hydrogen atom from a metal methyl molecule, and so will have an activation energy that will change from compound to compound according to the electronegativity of the central atom; but from Table 1 it is clear that no reflection of any change in activation energy is to be detected in the proportions of methane and ethane produced. Thirdly, it has been generally overlooked that an alternative methane-producing process can be postulated, namely:

$$CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5$$

Omission to consider this reaction is serious, because hydrogen abstraction should proceed with a lower activation energy from ethane than from the metal methyls. It is true that activation energies have been estimated for only a few of these compounds in metathetical reactions with methyl radicals, but as far as the available evidence extends, it supports this expectation. The estimates for dimethylmercury are compared with the surprisingly sparse data for ethane in Table 3. The figures for dimethylmercury are in rather poor agreement, but apart from Gomer and Noyes's work, which has been questioned by other workers and also rests on rather bold assumptions as to reaction mechanism, the consensus of opinion is that the activation energy lies in the region 11—15 kcal. Inasmuch as the estimates rest on formation of methane without correction for the methane-producing process $CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5$, they will be low, so that the true activation is more likely to lie in the region 13—15 than 11—13 kcal. The only estimate for the corresponding reaction with dimethylcadmium [21] likewise places the activation energy at ~14 kcal. Relative to hydrogen-abstraction reactions for simple hydrocarbons these figures are high, but that is not surprising for methyl compounds of elements of such low electronegativity as cadmium and mercury. The less electrophilic the central atom, the more will it release electrons to the attached alkyl groups, so increasing the density of the electron cloud surrounding the methyl groups. This, by enhancing the potential barrier to be surmounted by the attacking methyl radical, will serve to increase the energy of activation of the metathetical process. With ethane the energy of activation is only 8—10 kcal. (Table 3), that is to say, some 5 kcal. lower.

TABLE 3. *Activation energies of hydrogen-abstraction reactions.*

Activation energy (kcal.)	Investigators	Activation energy (kcal.)	Investigators
(*a*) Reaction $CH_3 + Hg(CH_3)_2 \longrightarrow CH_4 + \cdot CH_2\cdot Hg\cdot CH_3$:			
11·6	Thompson and Linnett [14]	11	Gomer and Noyes [16] as corrected by Phibbs and Darwent [17]
13	Cunningham and H. S. Taylor [7]		
13—14	Saunders and H. A. Taylor [15]	10·8	Rebbert and Steacie [4]
9	Gomer and Noyes [16]	15	Yeddanapalli *et al.*[8]
(*b*) Reaction $CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5$:			
8·3	Smith and H. S. Taylor [18]	10·4	Trotman-Dickenson and Steacie [19, 20]

This circumstance will mean that the latter reaction is very much faster, especially since ethane will as the simpler molecule also have a decidedly more favourable steric factor. Consequently, in the competition for methyl radicals, ethane, which is inevitably present where methyl radicals are to be found, would be expected to account for the fate of an overwhelming proportion of radicals. We conclude therefore that it is the presence of ethane which is largely responsible for formation of methane, and at not too high temperatures will be virtually exclusively so. Other reasons for this conclusion, based on observations on the behaviour of decomposing dimethylmercury, have been presented in detail elsewhere.[22] Now the same solution is seen to explain simply the otherwise surprising observation that almost all the metal methyls so far studied decompose in accordance with a first-order law. It also explains neatly the unexpected similarity in methane : ethane ratios produced by decomposition of the various compounds at a fairly low temperature.

The Proposed Mechanism.—It is now necessary to draw up a new mechanism to account for the fate of the methyl radicals liberated by those metal methyl compounds that decompose in accordance with a first-order law. A mechanism is possible in which the methane is produced entirely from the methyl radicals, not on the first collision, but in a series of steps, of which the following are probably the most important :

$$\begin{array}{rll} CH_3 + CH_3 \longrightarrow & C_2H_6 & E = 0 \text{ kcal.} \\ CH_3 + C_2H_6 \longrightarrow & CH_4 + C_2H_5 & E = 8\text{—}10 \text{ kcal.} \\ CH_3 + C_2H_5 \longrightarrow & C_3H_8 & E = 0 \text{ kcal.} \\ CH_3 + C_3H_8 \longrightarrow & CH_4 + C_3H_7 & E = 6\text{—}8 \text{ kcal.} \\ C_3H_7 \longrightarrow & CH_3 + C_2H_4 \text{ (polymerises)} & \end{array}$$

All of these steps are associated with comparatively low activation energies and are therefore reasonable. The propane formed at an intermediate stage has actually been observed in traces,[4] but will have no opportunity to build up a sizeable concentration as it reacts

[14] Thompson and Linnett, *Trans. Faraday Soc.*, 1937, **33**, 874.
[15] Saunders and H. A. Taylor, *J. Chem. Phys.*, 1941, **9**, 616.
[16] Gomer and Noyes, *J. Amer. Chem. Soc.*, 1949, **71**, 3390.
[17] Phibbs and Darwent, *Canad. J. Res.*, 1950, *B*, **28**, 395.
[18] Smith and H. S. Taylor, *J. Chem. Phys.*, 1939, **7**, 390.
[19] Trotman-Dickenson and Steacie, *J. Amer. Chem. Soc.*, 1950, **72**, 2310.
[20] Trotman-Dickenson, Birchard, and Steacie, *J. Chem. Phys.*, 1951, **19**, 163.
[21] Anderson and H. A. Taylor, *J. Phys. Chem.*, 1952, **56**, 498.
[22] Long, *Trans. Faraday Soc.*, 1955, **51**, 673.

with methyl radicals very much faster than does ethane, which unlike propane possesses no secondary hydrogen atoms. The resultant propyl radicals are known to be unstable (as are all higher alkyl radicals) and, at the temperatures employed, to split up spontaneously in the manner indicated, while ethylene polymerises in the presence of free radicals.

It is now possible to see why the methane : ethane ratio hardly varies for metal alkyls decomposing at widely different absolute rates, even though formation of methane is of first order with respect to methyl, while formation of ethane (owing to its heterogeneous and homogeneous components) has an order lying between 1 and 2 with respect to methyl. For static systems the temperature is so chosen that a suitable fraction of the alkyl decomposes during a conveniently measurable run, of duration usually 1—10 hours. The rates of release of methyl radicals will therefore only vary over a restricted range lying within a single power of ten from the mean. But since the faster the ethane is formed the faster it will be consumed by other methyl radicals, what matters is not its initial rate of formation, but its equilibrium concentration (for most of it is consumed). And since this is low at the temperature employed in the static system (say 320°), a moderate change in the rate of radical release will in practice affect the equilibrium concentration by at most a few per cent. It follows that, to a first approximation, the methane : ethane ratio will be independent of the initial concentration and percentage decomposition as well as of the nature of the decomposing alkyl, a state of affairs not predicted by any of the older mechanisms.

More direct evidence against the manner of methane formation assumed by other workers is to be found in the pyrolysis study by Gowenlock, Polanyi, and Warhurst, who used a flow technique.[23] They observed that the addition of ethane greatly increased the proportion of methane formed, but did not affect the rate of decomposition of dimethylmercury. Although the authors offer no explanation, this observation not only suggests an important reaction between methyl radicals and ethane (as now proposed), but demonstrates that hydrogen-abstraction from dimethylmercury by methyl radicals does *not* occur to a measurable extent; and since this is true at 552°, it will also hold for the lower temperatures employed in static systems.

It is not claimed that the foregoing mechanism represents the complete picture embracing all the steps. Evidence for these and other, probably less important, processes—such as $CH_3 + C_2H_5 \longrightarrow CH_4 + C_2H_4$ (polymerises); $C_2H_5 + C_2H_5 \longrightarrow C_4H_{10}$ *or* $C_2H_6 + C_2H_4$ (polymerises); $CH_3 + C_4H_{10} \longrightarrow CH_4 + C_4H_9$; $C_4H_9 \longrightarrow C_2H_5 + C_2H_4$ (polymerises) *or* $CH_3 + C_3H_6$ (polymerises)—is discussed more fully elsewhere[22] for the specific case of dimethylmercury. It is striking support for the theory that the different trains of reasoning now advanced lead to essentially identical conclusions.

The net effect of all these processes, whatever the relative importance of the possible paths, is the conversion of $2CH_3$ into $CH_4 + CH_2$ (polymerised); and here further support for the mechanism is to be found in the observation that methane and a relatively non-volatile CH_2 polymer are the principal products obtained in essentially equivalent amounts in the pyrolysis of dimethylmercury[1,7] and dimethylcadmium.[2] Residual ethane and ethylene are also to be expected and are in fact observed. Thus in the case of dimethylmercury, the composition of the gaseous products observed by Laurie and Long[1] at 303° was : CH_4, 93%; C_2H_6, 3%; C_2H_4, 4%. These figures correspond to a methane : ethane ratio of $>30:1$, which is much higher than that observed by other workers. Thus Yeddanapalli, Srinivasan, and Paul[8] found 5·8 : 1 at 305·5° and Pellin[9] 3·1 : 1 at 312°. The main reason for this discrepancy probably lies in the nature of the surface. Thus Pellin did not clean his reaction vessel between the individual runs whereas Yeddanapalli *et al.* did, while Laurie and Long took the further precaution of baking it out under vacuum for 1 hr. at 350°. The importance of this procedure is to be stressed. The recombination of methyl radicals to form ethane is partly a wall reaction, so that a surface which is not scrupulously clean would affect the *fate* of the methyl radicals (though not the rate of their production by a homogeneous unimolecular process) in trapping larger numbers and favouring ethane formation against that of methane. The inference is that surface effects are to a greater or smaller extent responsible for such irregularities in the methane : ethane

---

[23] Gowenlock, Polanyi, and Warhurst, *Proc. Roy. Soc.*, 1953, *A*, **218**, 269.

ratios as are apparent in Table 1. But for these the concordance would doubtless be even more striking. (At higher temperatures it is apparently less important to bake out the reaction vessel, as shown by the close agreement of the results of Laurie and Long [1] at 346° with those of Cunningham and H. S. Taylor [7] at 348°.)

The foregoing mechanism relates solely to temperatures less than 340°. Above this temperature a new process becomes important, as shown by a decrease in the methane : ethane ratio (Table 2); Laurie and Long [1] found evidence for a change in the mechanism at or very close to this temperature, in that the slope of the Arrhenius plot for the decomposition of dimethylmercury changed sharply between 333° and 343°. There is at present not sufficient evidence to indicate the nature of this new process, but the experimental data of Pellin [9] and of Gowenlock *et al.*[23] indicate that for dimethylmercury it is not the establishment of a radical chain mechanism in the region 350—600°. At still higher temperature it is probable that the metal methyl molecules generally play a more complicated role in the decomposition in "static" systems than that of merely splitting off methyl radicals. This is strongly implied by the erratic methane : ethane ratio above 400° (Table 1).

The author is indebted to the Department of Scientific and Industrial Research for a Special Grant.

THE UNIVERSITY, EXETER.

[*Received, January* 16*th*, 1956.]